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Water Transport in Bicontinuous, Phase-Separated Membranes Made from Reactive Block Copolymers

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14. ABSTRACT
Heat buildup and the effective lifespan of current chemical agent protection for military personnel are still concerns. A semipermeable membrane that allows sweat to escape a chemical protection garment, while rejecting chemical agents, would provide a potential solution for both of these issues. Few semipermeable membranes transport water vapor at a sufficient rate to cool a Soldier working at moderate levels of effort, and the mechanical properties of these materials are also of concern. Membranes fabricated from reactive block copolymers and a small molecule cross-linker using ring-opening metathesis chemistry were tested for their water transport properties. These materials were found to transport water faster than current commercially available membranes at lower humidity levels. The mechanical properties of the membrane still limit its use as a garment in chemical agent protection.

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ionomer, membrane, water vapor, cocontinuous, bicontinuous

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Contents

List of Figures

List of Tables

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1. Introduction

Recent sarin attacks and United Nations confiscation of mustard gas in Syria has reaffirmed chemical agent protection as a priority among those responsible for the safety of US military personnel. The current standard of chemical agent protection, the Joint Service Lightweight Integrated Suit Technology employs 3 layers of open-cell polyurethane foam impregnated with activated carbon, a design that allows perspiration to evaporate while chemical agents are adsorbed onto the activated carbon.[1,2] However, heat buildup within the suit remains an issue, and activated carbons can adsorb limited quantities of chemical agent before they lose effectiveness. Therefore, new semipermeable membrane barrier materials that could reject chemical agents but allow sweat to pass through are being investigated.

NEXAR, the current highest performing semipermeable membrane material, developed by Kraton Polymers LLC, is a pentablock copolymer membrane in which the third (center) block consists of ionically charged, sulfonated polystyrene.[3] This ionic phase is exceptionally hydrophilic and provides the water transporting phase of the membrane. The other blocks consist of hydrophobic styrene, hydrogenated isoprene, or hydrogenated butadiene, which provide mechanical integrity for the membrane. These 2 hydrophobic and hydrophilic phases are microphase-separated with domain sizes of approximately 100 nm.

Our investigations were guided by this motif of microphase-separated and bicontinuous ionic and hydrophobic domains while exploring new ionic groups and methods for producing this microphase-separated morphology in a quick and reproducible manner that avoids the difficult synthetic challenges of living anionic polymerization. The performance of our new membrane was compared with that of NEXAR and a commercially available cation-containing membrane, Tokuyama A201, under the same conditions.

2. Experimental

2.1 Material Synthesis

Semi-permeable membranes designated “C30D70-1.7” were synthesized via a modified literature procedure, and the synthetic methodology and detailed membrane characterization have been published elsewhere.[4]

2.2 Macro Chain Transfer Agent (CTA)[5]

(Vinylbenzyl)trimethylammonium chloride (2.07 g, 9.79 mmol),
2-(Dodecylthiocarbonothioylthio)propanic acid (DoPAT) (72.7 mg, 0.207 mmol), and

azobisisobutyronitrile (AIBN) (8.5 mg, 0.0518 mmol) were dissolved in 10 mL of ethanol. The mixture was degassed by 3 freeze-pump-thaw cycles, refilled with nitrogen, and then heated to reflux.

After 16 h of refluxing under nitrogen, the mixture was precipitated into acetone and filtered. The yellow solid was washed with acetone and then dried over calcium sulfate for 24 h at 1-mm mercury (Hg). Yield: 1.938 g (90.4%). ^{1}H NMR (MeOH-d_4, 600 MHz, δ): 7.44-6.63 (m, Ar-*H*), 4.72-4.53 (m, N-CH_2), 3.10 (br s, N-CH_3), 1.67 (m, -CH_2-C*H*-), 1.27 (s, DoPAT CH_2), 0.89 (t, $^{3}J_{HH}$ = 6.6 Hz, DoPAT CH_3). M_n = 11 kg mol^{-1} by nuclear magnetic resonance (NMR).

2.3 PA-b-XS

Macro CTA (600 mg), monomer 2 (386 mg, 1.72 mmol), styrene (418 mg, 4.01 mmol), and AIBN (2.2 mg, 0.0136 mmol) were dissolved in 1.9 mL of dioxane and 5.6 mL of n-propanol. The mixture was degassed by sparging with nitrogen for 15 min and then heated to reflux. After 16 h refluxing under nitrogen, the mixture was concentrated via rotary evaporation and precipitated into diethyl ether. The resulting yellow solid was washed with ether, redissolved into ethanol, and then precipitated a second time to remove traces of unreacted monomer. The polymer was then dried over calcium sulfate for 24 h at 1-mm Hg. Yield: 681 mg (48.5%). ^{1}H NMR ($CDCl_3$, 600 MHz, δ): 7.33-6.61 (m, Ar-*H*), 6.07 (br s, endo C*H*=C*H*), 5.83 (br s, exo C*H*=C*H*), 4.71-4.53 (m, Ar-CH_2-O and Ar-CH_2-N), 3.10 (br s, N-CH_3), 1.81-1.42 (m, -CH_2-C*H*-), 1.28 (s, DoPAT CH_2), 0.89 (br s, DoPAT CH_3), 0.48 (br s). Analysis found for PA-b-XS: C, 67.08; H, 8.68; N, 4.75. M_n = 15.2 kg mol^{-1} by NMR.

2.4 Membrane Casting Procedure, Representative Example

A mixture consisting of 221 mg of a premade 70:30 by weight dicyclopentadiene (DCPD):carbon monoxide (CO) was weighed into a 5-mL flask with a stir bar. Then 279 mg of PA-b-XS was added, followed by 1.5 mL of ethanol. The flask was stirred for 10 min to ensure a homogenous solution. Then 3.2 mg of Grubbs second-generation catalyst, was dispersed into a minimal volume (4–5 drops) of ethanol. The catalyst solution was then added to the polymer solution while stirring rapidly. The solution was stirred for 30 s, filtered onto a glass plate with kapton tape defining a 2.5- × 2.5-inch casting area, and then covered with a large petri dish for 16 h. Water was added, and the substrate was gently heated with a heat gun to release the film from the glass plate. The slightly yellow membranes were then peeled from the surface and washed with water, acetone, ethyl acetate, acetone, and finally water. Membranes were then immersed in water for 24 h before use.

2.5 Water Transport Measurements

Figure 1 shows the configuration and sample cells for testing membranes. A dry nitrogen stream was sent through a frit to a dual-bubbler, where the stream was bubbled through water until saturated. To verify that the stream was indeed saturated with vapor, the number of bubblers through which the saturated stream would pass was increased until no further change was

observed in the detector signal. Two bubbler columns were used in series to compensate for the heat of evaporation and retain the desired temperature and saturation level. The saturated stream was combined with a dry nitrogen stream to regulate the activity of the feed stream being sent to the test cell. A dry sweep was fed to the permeant side of the film and toward a thermal conductivity detector (Agilent MicroGC 3000), which sampled from the sweep stream every 2 min. The bubbler and test cell were enclosed in a temperature-controlled polycarbonate chamber regulated with an Airtherm from World Precision Instruments. Gas flow rates were regulated with electronic mass flow controllers (MKS Incorporated).

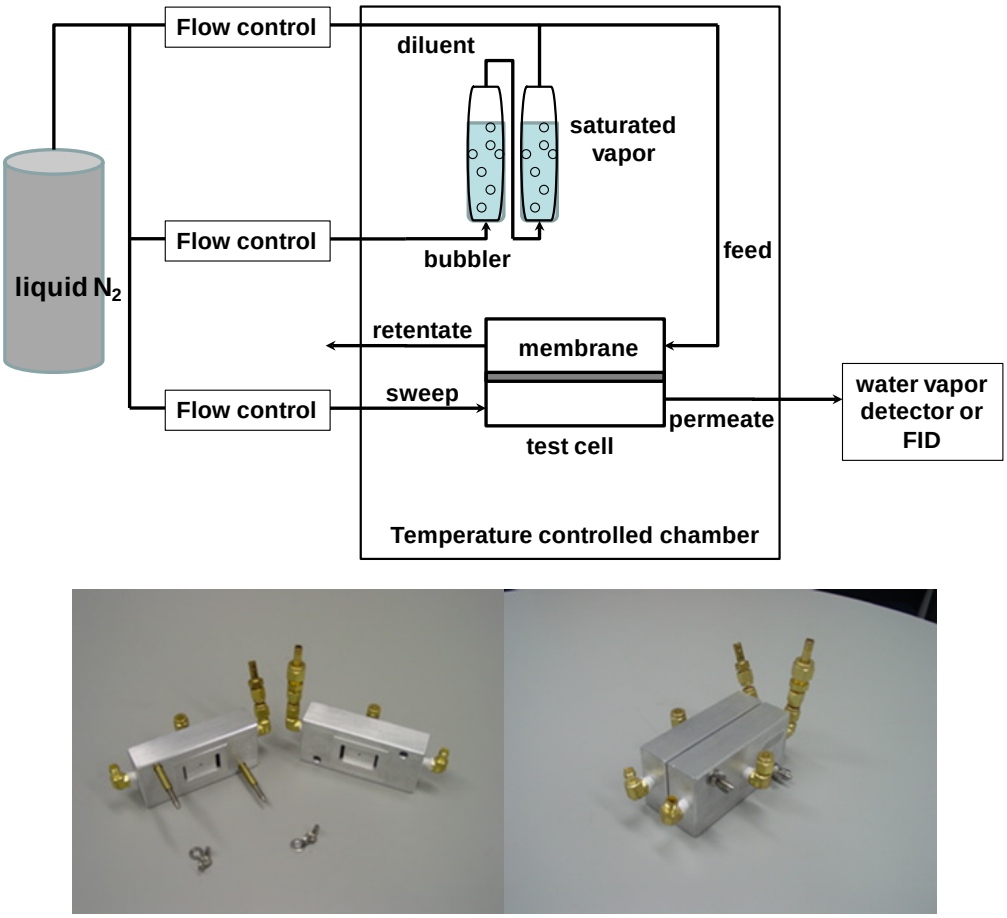

Fig. 1. Experimental flow diagram setup and test cell

Experiments were performed at 35 °C to mimic skin temperature, and the activity of the feed stream was varied between 0.1 and 0.9, calculated from the ratio of the saturated and dry feed flows. Both feed and sweep streams were kept at 500 cm^3 to reduce the boundary layer resistance of the test cell. The test cell shown in Fig. 1 was machined from an aluminum block and had an exposed membrane area of 0.75 × 1.25 cm, or 6.0 cm^2. The cell consisted of a raised edge surrounding the open area (76 cm high × 0.64 cm wide) with which to clamp down on the film and provide a seal. The flow channels of the cell were made at a 30° angle to improve the sweep along the membrane surface. The streams were flowed in counter-current fashion to minimize

the transmembrane concentration difference along the length of the test cell. Ports were located on either side of the sample to measure the pressure drop across the film if needed and adjust it if necessary. However, there was no pressure difference across the film in this series of experiments.

3. Results

C30D70-1.7 was synthesized from a block copolymer crosslinked during film casting with DCPD and cyclooctene via Grubbs second-generation metathesis catalyst (Fig. 2). The block copolymer was synthesized via reversible addition-fragmentation chain-transfer (RAFT) polymerization in 2 steps, synthesizing the ionic block first due to ease of purification. The diblock copolymer PA-b-XS was then dissolved into ethanol with a 70:30 by weight ratio of dicyclopentadiene and cyclooctene, Grubbs second generation metathesis catalyst was added, and the mixture was filtered and cast on a glass substrate (Fig. 3). A summary of the film properties can be found in Table 1.

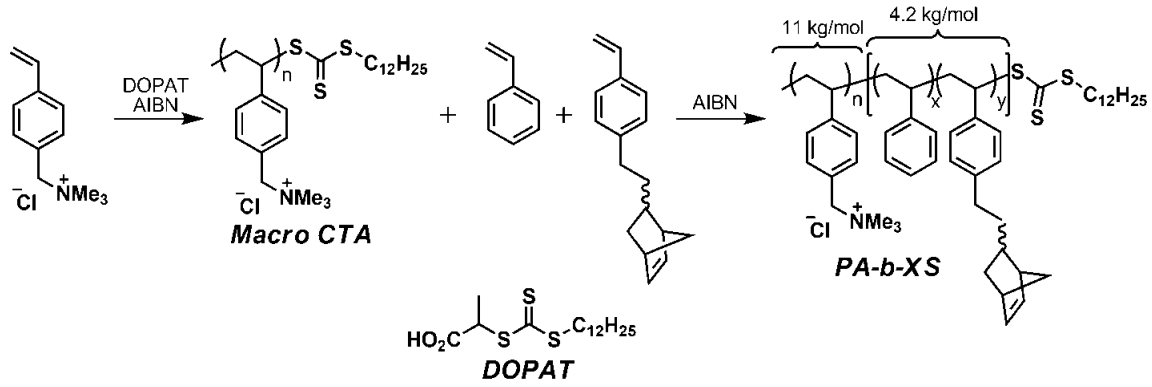

Fig. 2 Block copolymer synthesis via RAFT polymerization

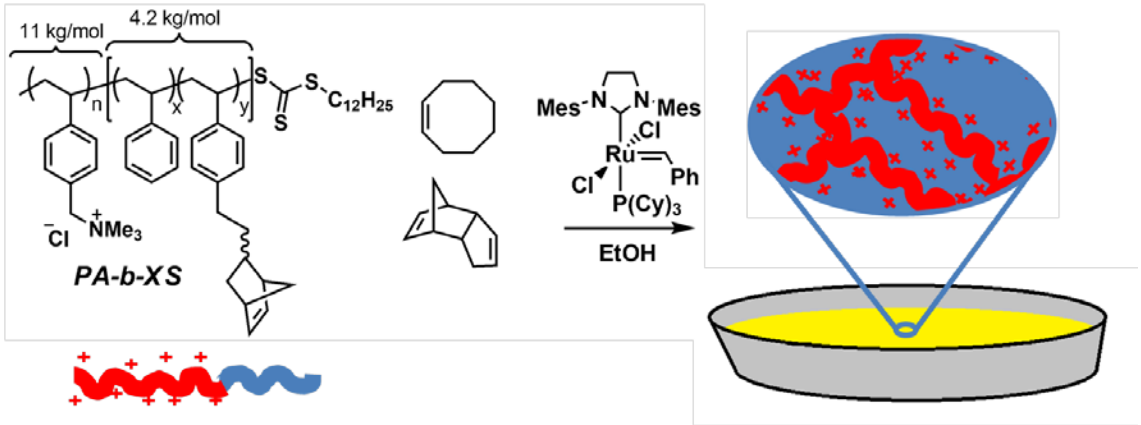

Fig. 3 C30D70-1.7 films are crosslinked while cast by Grubbs second-generation catalyst

Table 1 Performance attributes of C30D70-1.7 films

Water Uptake at 22 °C (mass %)	Ion Exchange Capacity (meq g^{-1})	Young's Modulus at 80 °C, 85% RH (MPa)	0.2% Yield Stress at 80 °C, 85% RH (MPa)	Chloride Conductivity at 22 °C in Water (mS cm^{-1})
84.2%	1.7	5.8	0.55	18.4

Note: RH = Relative humidity

The film thickness of C30D70-1.7 was fairly uniform at 5.4 mil. The thickness was measured after exposure to 90% humidity for 24 h and then ambient conditions. No difference was discerned. The mass change from 90% to 40% relative humidity in Fig. 4 shows the flux of water vapor over time as the feed activity was changed. While the flux stabilized fairly quickly at as the feed activity was changed, changing the activity to 0.4 resulted in a decrease, and then a slow increase over time, requiring roughly 2 days to equilibrate. Reducing the activity to 0.2 resulted in no detectable flux of water vapor.

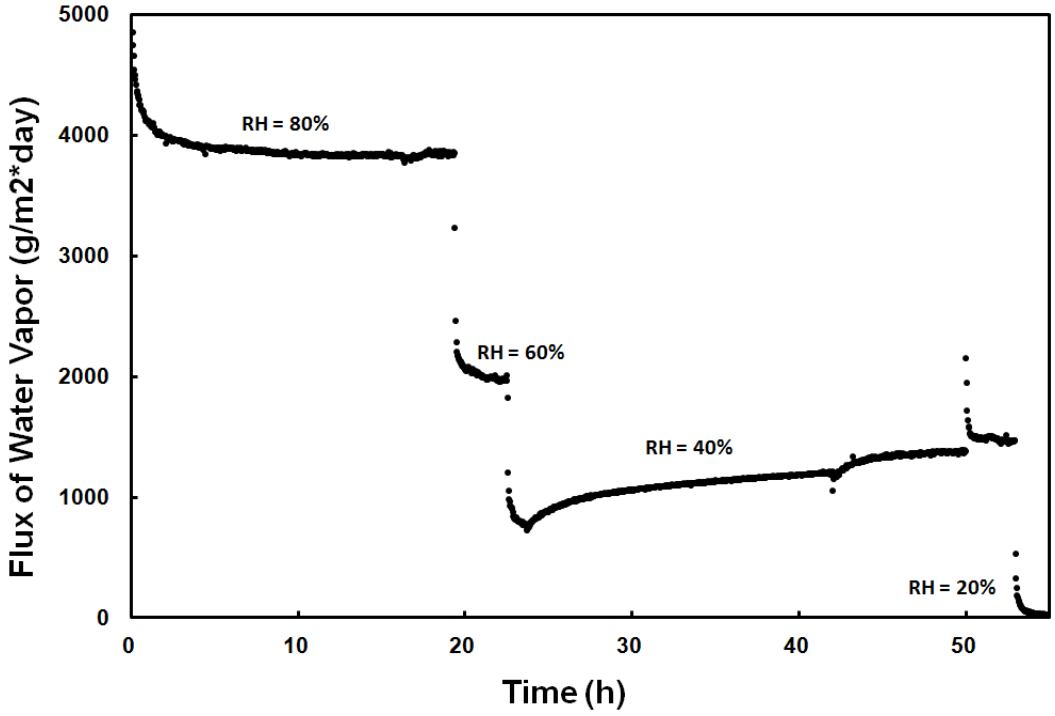

Fig. 4 Raw flux vs. time for C30D70-1.7 at 35 °C

Table 2 and Fig. 5 show a comparison of C30D70-1.7 with the current standard, NEXAR MD9200, and to the current standard alkaline exchange membrane, Tokuyama A201. The flux values are normalized for thickness, and the boundary layer resistance of the test cell subtracted. C30D70-1.7 performs better than the Tokuyama A201 commercially available cationic membrane, and the water vapor flux of the C30D70-1.7 film is higher than the NEXAR film at an activity of 0.4. However, by an activity of 0.6, the flux of the NEXAR film surpasses that of C30D70-1.7, while being more mechanically robust and thinner than the C30D70-1.7 membrane.

Table 2 Water vapor flux of membranes tested at 0.8 activity and 35 °C

Membrane	Average Thickness (mil)	Flux (g µm m^{-2} min^{-1})
C30D70-1.7	5.4	579
NEXAR MD9200	2.3	655
Tokuyama A201	1.8	320

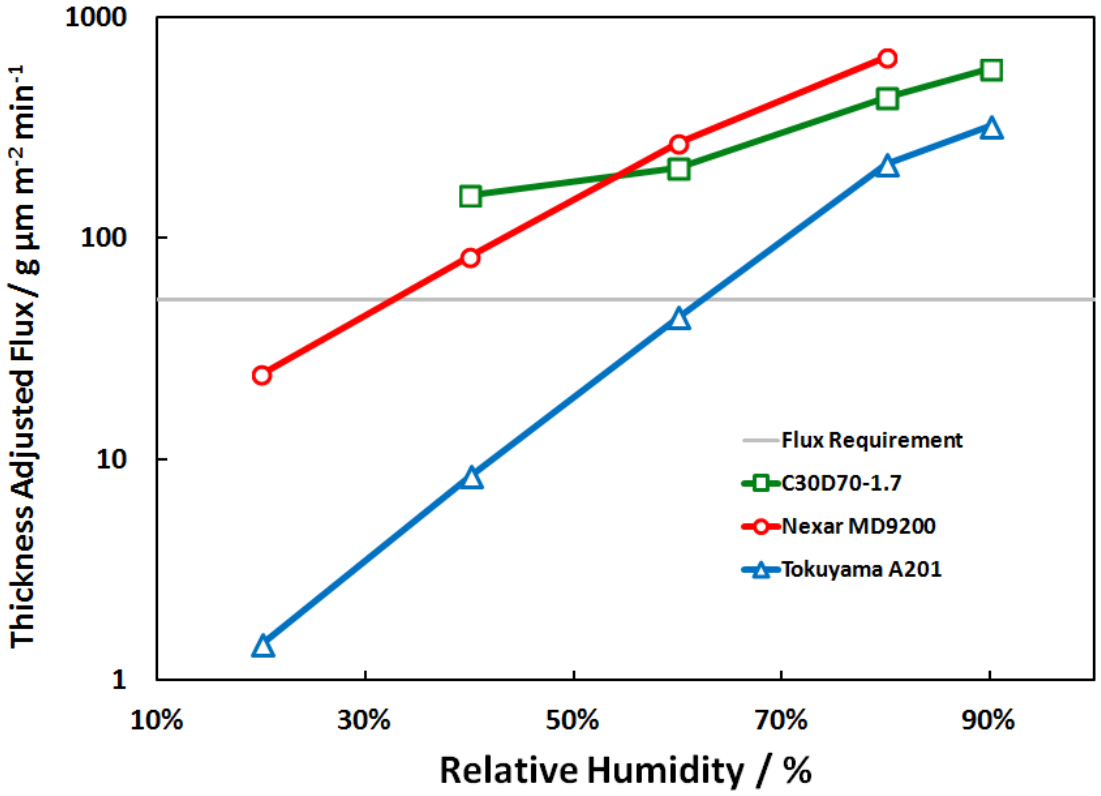

Fig. 5 Normalized flux vs. relative humidity for C30D70-1.7, Tokuyama A201, and Nexar MD9200 membranes at 35 °C. The gray line represents the typical sweat production for a Soldier performing at a medium work rate.

The C30D70-1.7 films also became brittle at very low humidity, cracking in the test cell. These films have been shown to have significant volumetric changes when going from wet to dry conditions. The shrinkage of the film while clamped into the test cell may have caused sufficient stress to crack the films when transitioning from high to low humidity. Clamping the film when dry and then hydrating the film can prevent breakage, but the key finding is that, qualitatively, these films do not have sufficient mechanical properties to withstand the rigors of typical wear as a protective barrier. Further increasing the molecular weight of PA-b-XS, decreasing the quantity of DCPD in the film, and other formulation optimizations are currently being pursued to increase the mechanical durability of these films.

4. Conclusions

Despite the promising water vapor transport performance of the C30D70-1.7 membranes, the mechanical properties of these membranes are still lagging behind the commercially available membranes and will need to be improved to be employed as a protective barrier material. The higher performance at low humidity levels should also be investigated further, as insights into improving transport at lower humidity levels may prove useful for the design of other membranes.

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